

REMARKS/ARGUMENTS

Favorable reconsideration of this application as presently amended and in light of the following discussion is respectfully requested.

Claims 1, 2, 4-6, 13-15, 17, and 27-31 are pending in this case. Claims 1 and 13 are amended and Claims 3 and 16 are canceled without prejudice or disclaimer by the present amendment. As amended Claims 1 and 13 are supported by the original claims, no new matter is added.

In the outstanding Official Action, Claims 1, 3-5, 13, and 15-17 were rejected under 35 U.S.C. §102(b) as anticipated by Ito (Japanese Patent Publication No. 07-037712). However, Claims 2 and 14 were objected to as being dependent on a rejected base claim, but otherwise was indicated as including allowable subject matter if re-written in independent form. Claims 27-31 were allowed.

Applicants gratefully acknowledge the allowance of Claims 27-31 and the indication that Claims 2 and 14 include allowable subject matter.

It is initially noted that Claims 1 and 13 are amended to include the subject matter of Claims 3 and 16, respectively. As the subject matter of Claims 3 and 16 was previously considered, it is respectfully requested that the present amendment under 37 C.F.R. §1.116 be entered and considered.

With regard to the rejection of Claim 1 under 35 U.S.C. §102(b) as anticipated by Ito, that rejection is respectfully traversed.

Amended Claim 1 recites in part, "wherein said insulating layers or said embedding material are made of either resin or a composite material which is made by mixing functional material powder into the resin."

The outstanding Office Action cited the insulator 3 of Ito made of SiO<sub>2</sub> as describing this feature. However, it is respectfully noted that SiO<sub>2</sub> is not a resin, and is not a composite

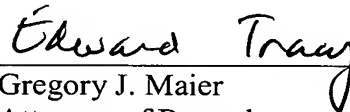
material made by mixing functional material powder into a resin. For example, the enclosed excerpt from the Fourth Edition of the Kirk-Othmer Encyclopedia of Chemical Technology states that a resin is a mixture of monocarboxylic acids, hydrocarbons, and saponifiable esters.<sup>1</sup> It is respectfully submitted that SiO<sub>2</sub> is not one of these components of a resin, nor is SiO<sub>2</sub> itself a resin. Thus, insulator 3 of Ito made of SiO<sub>2</sub> is not "made of either resin or a composite material which is made by mixing functional material powder into the resin" as recited in Claim 1. Consequently, as Ito does not teach each and every element of amended Claim 1, Claim 1 (and Claims 2 and 4-6 dependent therefrom) is not anticipated by Ito and is patentable thereover.

Amended Claim 13 recites similar elements to amended Claim 1. Accordingly, Claim 13 (and Claims 14, 15, and 17 dependent therefrom) is patentable over Ito for at least the reasons described above with respect to Claim 1.

Accordingly, the outstanding rejections are traversed and the pending claims are believed to be in condition for formal allowance. An early and favorable action to that effect is, therefore, respectfully requested.

Respectfully submitted,

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<sup>1</sup>See the Fourth Edition of the Kirk-Othmer Encyclopedia of Chemical Technology, Volume 21, page 293 (composition), copy enclosed.

KIRK-OTHMER

ENCYCLOPEDIA OF  
**CHEMICAL**  
**TECHNOLOGY**

FOURTH EDITION

VOLUME **21**

RECYCLING, OIL  
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SILICON

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## RESINS, NATURAL

Natural resins are generally described as solid or semisolid amorphous, fusible, organic substances that are formed in plant secretions. They are usually transparent or translucent yellow-to-brown colored, and are soluble in organic solvents but not in water. The principal uses for natural resins are in varnishes, printing

inks, adhesives, paper size, and polymer compositions. The term natural resins includes tree and plant exudates, fossil resins, mined resins, and shellac. They often have been altered from their original state during isolation and processing. For some applications, the resins have been chemically modified to increase their industrial utility.

Natural resins, except for shellac, are mixed condensation products of naturally occurring terpenoids and flavonoids contained in trees. Shellac is a product of insect secretion. Molecular weights probably do not exceed 10,000. The resins do not exhibit simple melting or boiling points, although they do have a predominant glass-transition temperature,  $T_g$ . The  $T_g$  of natural resins ranges from about 0 to 100°C. The relatively high  $T_g$  is caused by the rigid, cyclic structure of the resin. Depending on its  $T_g$ , a natural resin at room temperature may be a brittle glass, or it may be flexible and extensible.

Natural resins were probably known to early people, who recognized them as exudates from trees. Collection and use of these resins have been recorded by early Roman and Greek historians. Many products have been collected by the same methods throughout history to the present time. However, increased labor costs and competition from synthetic resins have reduced the demand for some natural resins, so they have become less available. In other cases, such as that of rosin, the traditional collection of gum from trees has been supplemented or replaced by isolation from other sources, such as paper pulping and tree stumps.

### Rosin and Modified Rosins

Rosin and associated products obtained from pine trees have been used for hundreds of years to caulk the bottoms of wooden sailing vessels and to lubricate the lines. These materials are known as naval stores because of this practice.

**Production.** Rosin is isolated from pine trees, principally from longleaf *Pinus palustris*, slash *Pinus ellioti*, and loblolly pine *Pinus taeda*. The products are known as gum, wood, or tall oil rosin, based on the method of isolation and the source.

In the gum rosin process, pine trees are wounded to stimulate the flow of gum. V-shaped slashes are cut through the bark, and the exudate is collected in a bucket below the slash. Production is stimulated by painting sulfuric acid on the slashes. The oleoresin (exudate) is separated by distillation into gum spirits of turpentine and gum rosin. The gum turpentine industry has decreased in importance in the 1990s because it is labor-intensive. The process is carried out in Russia, the People's Republic of China, Indonesia, Portugal, Brazil, and Mexico.

In the wood rosin process, rosin is isolated from aged pine stumps that have been left in fields cleared for farming or lumbering operations. The stumps are cut and shredded to pieces the size of matchsticks. The wood chips are then extracted with an appropriate solvent, eg, aliphatic or aromatic petroleum hydrocarbons or ketones. The extract is fractionally separated into nonvolatile crude rosin, volatile extractibles, and recovered solvent. The dark rosin is usually refined further to lighter-colored products using selective solvents or absorption.

Tall oil rosin is a by-product of paper manufacturing. Raw wood chips are digested under heat and pressure with a mixture of sodium hydroxide and sodium

sulfide. So are removed and fatty acids are treated with crude tall oil distillation.

The types and proportions of resins differ, and differences in properties are observed.

**Properties.** Rosins are amorphous and have a high molecular weight. The  $T_g$  of natural resins is higher than that of synthetic resins. The weight-average molecular weight is higher than the number-average molecular weight. The molecular weight distribution is broad.

**Chemical Properties.** Rosins are composed of terpenoids and flavonoids. They are soluble in organic solvents and are resistant to oxidation and reduction. They are also resistant to acids and bases.

**Uses.** Rosins are used in a wide variety of applications, including adhesives, coatings, and inks. They are also used in the production of resins and in the treatment of wood. Rosins are also used in the production of resins and in the treatment of wood.

**Modified Rosins.** Rosins can be modified by a variety of methods, including chemical and physical methods. Modified rosins are used in a wide variety of applications, including adhesives, coatings, and inks.

sulfide. Soluble sodium salts of lignin, rosin, and fatty acids are formed, which are removed from the wood pulp as a dark solution. The soaps of the rosin and fatty acids float to the top of the mixture, where they are skimmed off and treated with sulfuric acid to free the rosin and fatty acids. This mixture, known as crude tall oil (CTO), is refined further to remove color and odor bodies; fractional distillation separates the tall oil rosin acids from the fatty acids (see TALL OIL).

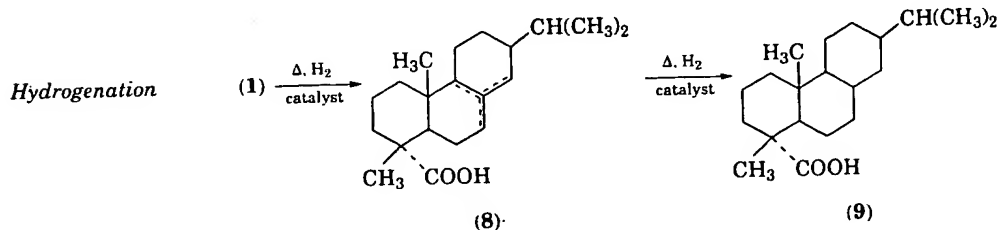
The three types of rosin perform differently because of different distributions of resin acids, as well as different types and quantities of impurities. These differences are reflected in end-use performance.

**Properties.** Rosin is a brittle, friable solid which has a  $T_g$  of ca  $30^\circ\text{C}$  and a ring and ball (R&B) softening point of ca  $75^\circ\text{C}$ . Although the average molecular weight is only about 300, its rigid cyclic structure results in a higher  $T_g$  than would be expected for an amorphous polymer of the same molecular weight. Heating above the softening temperature lowers viscosity sharply as a consequence of the low molecular weight.

Rosin is compatible with many materials because of its polar functionality, cycloaliphatic structure, and its low molecular weight. It has an acid number of ca 165 and a saponification number of ca 170. It is soluble in aliphatic, aromatic, and chlorinated hydrocarbons, as well as esters and ethers. Because of its solubility and compatibility characteristics, it is useful for modifying the properties of many polymers.

**Composition.** Rosin is primarily a complex mixture of monocarboxylic acids of alkylated hydrophenanthrene nuclei. These constituents, known as resin acids, represent about 90% of rosin. The resin acids are subdivided into two types, based on their skeletal structure. The abietic-type acids contain an isopropyl group pendent from the carbon numbered 13. The pimaric-type acids have a methyl and vinyl group pendent from the same carbon atom. Figure 1 shows the structure of typical resin acids; abietic acid,  $\text{C}_{20}\text{H}_{30}\text{O}_2$  (1) is predominant. The remaining 10% of commercial rosin consists of neutral materials that are either hydrocarbons or saponifiable esters. These materials are derived from resin acids by decarboxylation or esterification. Typical grades of tall oil rosin also contain about 2–5% of  $\text{C}_{18}$ – $\text{C}_{26}$  fatty acids.

**Modified Rosins.** Natural rosins are often modified to improve their stability to long-term aging and oxidative degradation. Pale color and color stability are also important. Stabilization methods involve the double bonds in the resin acid molecule that can form a conjugated system highly susceptible to degradation. The double bonds can be stabilized by hydrogenation, disproportionation, or polymerization. Hydrogenation stabilizes the rosin by eliminating



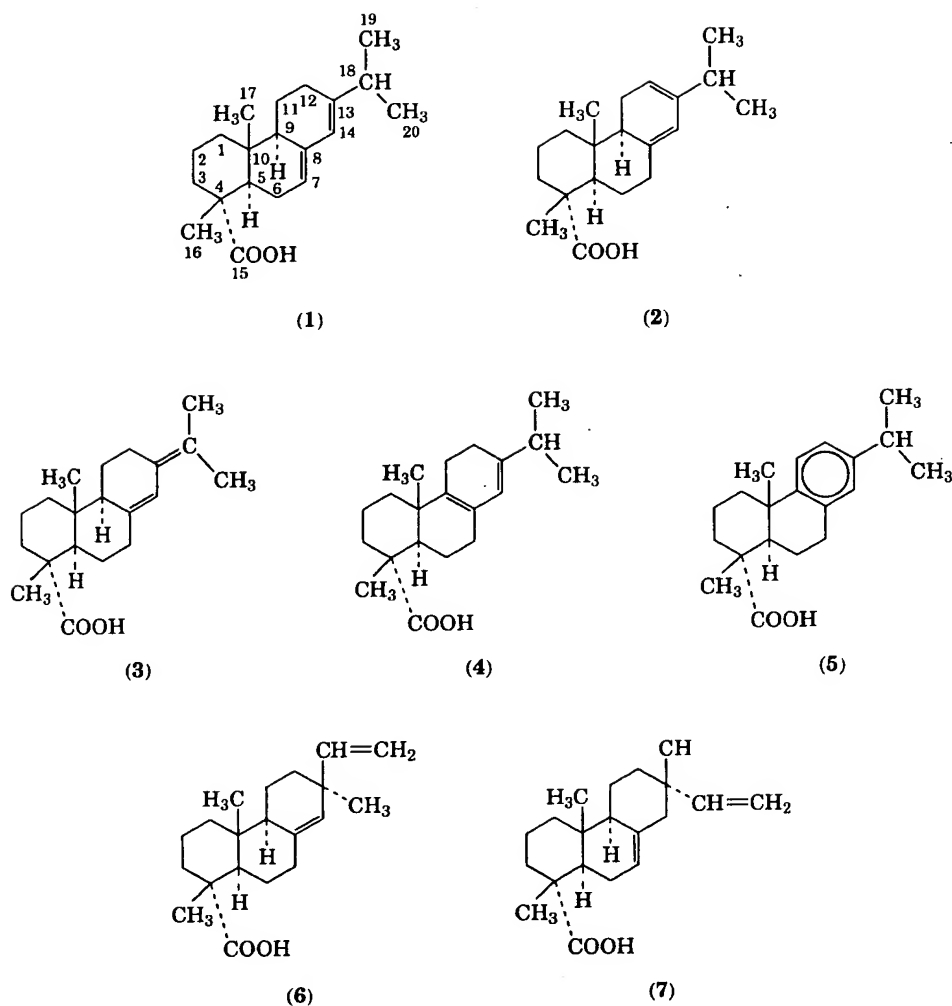
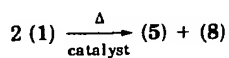


Fig. 1. Abietic-type acids include abietic acid [514-10-3] (1), levopimaric acid [79-54-9] (2), neoabietic acid [471-77-2] (3), palustric acid [1945-53-5] (4), and dehydroabietic acid [1740-19-8] (5). Pimaric-type acids are pimaric acid [127-27-5] (6) and isopimaric acid [5835-26-7] (7).

at least one of the double bonds; dihydroabietic acids (8) and tetrahydroabietic acid (9) are formed. Hydrogen also reacts with color bodies to stabilize the product further.

In disproportionation, rosin is heated over a catalyst to transfer hydrogen, yielding dehydro (5) and dihydro (8) resin acids. The dehydro acids are stabilized by the aromatic ring; the dihydro acids contain only an isolated double bond in place of the less stable conjugated double bonds.

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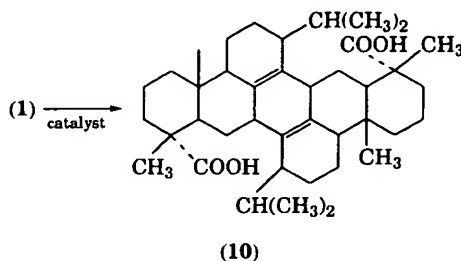
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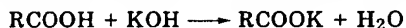
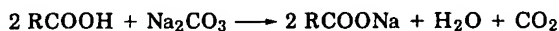
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Rosin is polymerized by acid treatment at elevated temperatures, whereby double bonds are eliminated by dimerization. Dimerized rosin (10) has a higher molecular weight and a correspondingly higher softening point. It is more stable because fewer double bonds remain and conjugation is reduced.

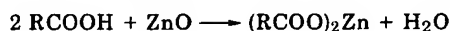
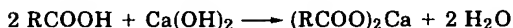


**Derivatives.** Most rosin products are sold as derivatives, which extends their utility. The carboxyl group or the double bonds are usually involved in the reactions.

The carboxyl group reacts with metal oxides, hydroxides, or salts to form rosin soaps or salts (resinates). The soaps of alkali metals, such as sodium and potassium, are useful in paper sizing and as emulsifiers in rubber polymeriza-

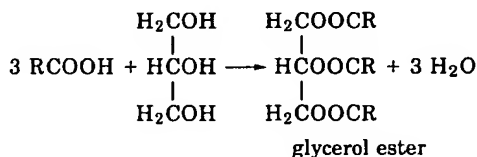


tion. The salts, primarily calcium and zinc resinate, are used in printing ink formulations. The carboxyl group is converted to the alcohol by catalytic

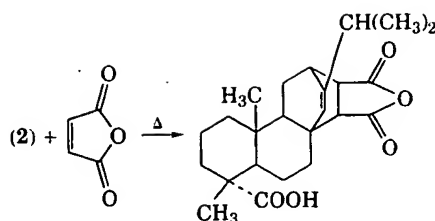


hydrogenation. Primary amines are prepared by amination to the amide, further dehydration to the nitrile, followed by hydrogenation to the amine.

The most important derivatives of the carboxyl group are formed by esterification with monohydric or polyhydric alcohols. Typical alcohols used include methyl alcohol, ethylene glycol, glycerol, and pentaerythritol. These rosin esters have a wide range of softening points and compatibilities.



The Diels-Alder reaction with dienophiles such as maleic anhydride or acrylic acid gives useful polycarboxylic acids, which can then be converted to metal salts or soaps or esterified to esters with high softening points.



**Uses.** The largest commercial use of rosin is in sizing paper to improve its water resistance, but it is being displaced by synthetic sizes. Paper size consists of rosin or modified rosins that have been partially saponified with sodium carbonate or sodium hydroxide. Sizes prepared from rosin may be modified with maleic anhydride to increase efficacy. Specialty paper is treated with stabilized rosins to minimize yellowing during aging. Sizes are used in concentrations of 0.1–3.0%. Aluminum sulfate (alum) (0.5–3.0%) increases the acidity of the paper pulp slurry. The sodium soaps of the rosin or modified rosins are precipitated as insoluble, positively charged aluminum mono- and diresinates, which are attracted to the negatively charged pulp fibers. They are retained in the paper mat when the water is removed. The hydrophobic aluminum resinate resists the penetration of water into the capillaries of the paper. Sizes consisting of 30–50% aqueous dispersions of rosin are also used. The alum–rosin interaction occurs on the surface of the pulp fiber.

Modified rosins, metal resinates, and resin acid esters find application in printing ink formulations. Rosin-derived resins dispersed in linseed oil are used as vehicles for letterpress inks. The resins provide specific adhesion, abrasion resistance, and gloss, and they improve pigment wetting and dispersion. Resins with high acid numbers are used as vehicles for flexographic inks, which are designed for printing on paper, metal, and plastic films. The resins provide flexibility, abrasion resistance, and gloss. Metal salts of rosins, modified rosins, and polymerized rosins are used in inexpensive gravure inks. In higher quality inks, rosin ester resins and phenolic-modified rosin esters provide hardness, gloss, and adhesion.

Rosin ester resins are used extensively in pressure-sensitive adhesives as tackifiers. The adhesive is formulated by blending the resin with a polymer in solution or as aqueous emulsions. Typical compositions may contain about 50% resin. The glycerol or pentaerythritol esters of stabilized rosins are often used because they are stable on aging.

Rosin, modified rosins, and derivatives are used in hot-melt adhesives. They are based primarily on ethylene–vinyl acetate copolymers. The rosin derivative is used in approximately a 1:1:1 concentration with the polymer and a wax. The resin provides specific adhesion to the substrates and reduces the viscosity at elevated temperatures, allowing the adhesive to be applied as a molten material.

Rosin ester resins are used as modifiers in the formulation of chewing gum. The rosin derivative modifies the physical properties of the polymer used, providing the desired masticatory properties. The glycerol ester of hydrogenated rosin is the predominant choice, because stabilized materials have improved aging resistance, which extends the shelf life of the gum.

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The soap of modified rosin has a long history as an emulsifier for the polymerization of styrene-butadiene rubber. The rosin soap remains in the rubber after polymerization and increases the tack between the plies of rubber required in the manufacture of tires.

### Traditional Natural Resins

Natural resins have been collected by hand throughout recorded history and used with minimal processing. They are reported to have been used in the arts, both in paints and for polishing sculptures, as early as 350 BC. Amber, the hardest of these resins, has been used as a gemstone from early Greek history to modern times. The electrical properties of amber were first recorded about 300 BC. Following is a description of commercial natural resins that are available in the United States.

**Manila Copal.** The Manilas are collected in Indonesia and the Philippines. They are soluble in alcohols and ketones, and insoluble in hydrocarbons and esters. The resins soften between 81–90°C and have acid numbers of 110–141. Principal uses are in coatings and varnishes.

**Pontianak.** This resin is a copal and is similar to the alcohol-soluble Manilas. It is partially fossilized, so it melts at a higher temperature. Softening points range from 99–135°C, and acid numbers from about 112–120. Pontianak [9000-14-0] is used in specialty coatings and adhesives.

**Dammar Resins.** These resins are tapped from trees in Indonesia and Malaysia. They have low acid numbers, typically 17–35, and softening points of between 67–75°C. They are soluble in aliphatic and aromatic hydrocarbons and in terpenes. Dammar resins [9000-16-2] are used primarily in protective-coating formulations. For use in lacquers, a small, high melting fraction of raw dammar must be removed to increase solubility in common lacquer solvents. The softening point of dewaxed dammar is 77–81°C, and its acid number ranges from 25–31. It is used as a spirit varnish over artistic oil paintings to shield against dirt.

**East India Resins.** The East India resins are related to the dammars, although they are older and harder. They are not obtained by tapping trees, but are collected where they are found, principally in Indonesia. Because they are semifossil resins, their softening points are high, ranging from about 110–130°C. The East India resins [9000-16-2] have low (20–30) acid numbers. They are soluble only in aryl hydrocarbons and hydrogenated aliphatic hydrocarbons, and are used primarily in coatings.

**Gum Elemi.** This resin, tapped from trees in the Philippines, contains a higher concentration of essential oils than other natural resins. It is a soft, sticky, plastic material that can be deformed manually. Gum elemi [9000-75-3] contains 20–25% essential oils, 13–19% acids, 30–35% resenes (condensed decarboxylated resin acids), and 20–25% terpenic resinols (condensed terpene alcohols). It has an acid number of 20–35 and a saponification number of 20–40. Gum elemi is a film-forming plasticizing resin used in lacquers.

**Sandarac.** This resin, which originates in Morocco, is a polar, acidic, hard resin with a softening point of 100–130°C, an acid number of 117–155, and a saponification number of 145–157. Sandarac [9000-57-1] is soluble in alcohols

and insoluble in aryl and aliphatic hydrocarbons. It is used in varnishes and lacquers for coating paper, wood, and metal.

**Mastic.** Most commercial mastic [61789-92-2] is collected on the Greek island of Chios, near the Turkish coast. It is a soft resin with a softening point of 55°C. It has an acid number of 50–70 and a saponification number of 62–90. It is soluble in alcohols and aryl hydrocarbons. Mastic is used in wood coatings, lacquers, adhesives, and printing inks.

**Other Resins.** Some resins that were important in earlier years have decreased in commercial significance because of scarcity and increased cost of collection. They are listed for the historical record.

**Kauri.** This fossil resin, classified as a copal, is found in the South Pacific, primarily in New Zealand. It formerly was used in protective coatings. It is still used in the Kauri-butanol test (ASTM D1133) to determine the volume of thinner that can be added to a varnish formulation without causing turbidity.

**Congo.** Another fossil copal, congo was developed by Belgian interests in the early 1900s in what is now Zaire. Production diminished when the Belgians left, and in the 1990s there is no organized isolation of congo in Zaire.

**Accroides.** This resin is collected in Australia in small quantities. Accroides has been used as a binder for wallboard, and in coatings and printing inks.

**Amber.** The hardest of all the resins, amber is still collected along the shores of the Baltic Sea. The pieces are polished to an attractive pale yellow-to-dark brown stone and made into ornamental objects.

### Natural Resins in Medicines, Flavors, and Fragrances

Some natural resins have been used for many centuries in medical applications, flavors, and fragrances. With advances in pharmacology, the medicinal uses of these resins have mostly disappeared. The only remaining significant application is the use of guaiac-impregnated paper to detect hemoglobin in stool. This widely used test is helpful in the early diagnosis of colorectal cancer. Use of the resins in cosmetics (qv) has come into question because of reports of contact dermatitis and skin sensitivity.

The natural resins described here are those that have been mentioned in technical literature; they can be identified by CAS Registry Numbers and Merck Index numbers (1).

Balm of Gilead [8022-26-2], also known as Balsam Mecca (Merck No. 958), obtained from Arabia and Abyssinia, has been used in perfumery. Balsam of Peru [8007-00-9] (Merck No. 959), obtained from Salvador, has been used in perfumery, skin ulcer therapy, and as an ingredient in chocolate flavoring. Balsam of Tolu [9000-64-0] (Merck No. 960), obtained from Venezuela and Colombia, has been used in perfumery, chewing gums, and as an expectorant. Copaiba [8001-61-4] (Merck No. 2511), obtained from the Caribbean and Brazil, has been used for treatment of cystitis, gonorrhea, and bronchial diseases, and as a diuretic. It has also been used as a varnish remover for oil paintings. Gum benzoin [9000-05-9] (Merck No. 4492), obtained from Indonesia and Thailand, has been used in ointments as a topical protector. Guaiac [9000-29-7] (Merck No. 4455), obtained from the Caribbean and the northern coast of South America, is still actively used

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as a reagent in testing for blood in stool. Myrrh [9000-45-7] (Merck No. 6251), obtained from East Africa and Arabia, has been used as a carminative and as an astringent for mucous membranes. Its ancient use as a perfume and as an incense is first described in the Bible. Olibanum [8050-07-5] (Merck No. 6792), also known as frankincense, is obtained from Arabia. It has been used as an ingredient of incense. Storax [8046-19-3] (Merck No. 8778), obtained from Turkey, has been used as a topical protector and an expectorant.

### Asphaltites

Mining operations are required to bring asphaltites to the market, principally for use in coatings and inks. They were formed in the same manner as oil and coal, below the surface of the earth from vegetation that had been subjected to high temperatures and pressures on a geological time scale. The most widely known asphaltite is gilsonite, which is found in the Uinta Basin in eastern Utah. Gilsonite has a softening point of 110–121°C. It has been used in protective coatings, battery cases, asphalt floor tiles, brake linings, and inks.

Glance pitch, or manjak, and grahamite are related to gilsonite, but have higher specific gravities. Glance pitch has the same softening point as gilsonite, 110–121°C. Grahamite is the highest melting of the asphaltites, softening at 176–315°C.

### Shellac

Unlike other natural resins, shellac [9000-59-3] is derived from the hardened secretion of the lac insect (species *Laccifer* (Tachardia) *lacca* Kerr (family Coccidae), also known as *Kerris lacca* (Kerr)). Shellac is a refined grade of the crude lac secretion and is the most widely known lac product. Therefore, shellac has been accepted as the common generic term. Over 50% of the world's supply is produced in the Indian provinces of Bihar and Orissa, with the remainder originating in adjacent areas of southeast Asia such as Sri Lanka, China, Thailand, and Myanmar.

The collection and use of lac by Indian aboriginal tribes probably predates recorded history. Ancient Greek and Roman writers were aware of lac. By the late fifteenth century, European craftsmen were attracted to the use of lac as a finish for cabinets and other furniture because of its gloss and luster. Lac became an important component of decorative and protective finishes by the nineteenth century. It is ironic that the success of shellac led to the synthetic resin industry. Baekeland developed phenolic resins while trying to find a substitute for shellac.

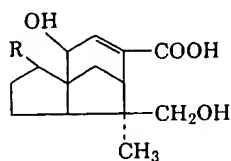
Lac is produced by the larvae of the lac insect, which secretes a coating composed of lac to protect it from weather and enemies. The secretions of neighboring larvae coalesce into one continuous coating over twigs of the host tree. This coating is harvested by cutting the twigs from the trees or by twisting the branches so that the resin falls off.

Raw lac is first treated to remove water-soluble carbohydrates and the dye that gives lac its red color. Also removed are woody materials, insect bodies, and trash. It is further refined by either hot filtration or a solvent process. In the heat process, the dried, refined lac is filtered molten through cloth or wire

screens to produce the standard grades of orange shellac. In the solvent process, lac is dissolved and refluxed in alcohol solvents, filtered to remove dirt and impurities, and concentrated by evaporation. The lac can be further decolorized in this process to produce very pale grades. Bleached shellac is prepared by treatment with dilute sodium hypochlorite and coalesced into slabs.

**Composition.** Shellac is primarily a mixture of aliphatic polyhydroxy acids in the form of lactones and esters. It has an acid number of ca 70, a saponification number of ca 230, a hydroxyl number of ca 260, and an iodine number of ca 15. Its average molecular weight is ca 1000. Shellac is a complex mixture, but some of its constituents have been identified. Aleuritic acid, an optically inactive 9,10,16-trihydroxypalmitic acid, has been isolated by saponification. Related carboxylic acids such as 16-hydroxy- and 9,10-dihydroxypalmitic acids, also have been identified after saponification. These acids may not be primary products of hydrolysis, but may have been produced by the treatment. Studies show that shellac contains carboxylic acids with long methylene chains, unsaturated esters, probably an aliphatic aldehyde, a saturated aliphatic ester, a primary alcohol, and isolated or unconjugated double bonds.

Cyclic sesquiterpenes having the cedrene skeleton have also been isolated. When  $R = \text{COOH}$ , this structure (11) has been named shellolic acid. Jalaric acid (11,  $R = \text{CHO}$ ) and laksholic acid (11,  $R = \text{CH}_2\text{OH}$ ) also have been isolated.



(11)

**Uses.** Synthetic resins have taken over a large share of the market for shellac. Unpigmented shellac is used on floors, woodwork, and paneling. White pigmented shellac is used as a primer-sealer for interior applications. Shellac is used as a protective coating for pharmaceuticals to maintain the potency of medication. Several coats of shellac glaze protect medication from the effects of stomach acids so that the medication is not released before the tablet reaches the intestines.

Candy is coated with shellac to seal in moisture and keep the product fresh. The coating provides a high gloss to the confection, which improves its appearance. Citrus fruits and some apples are often coated with shellac. This improves the appearance, while allowing the fruit to breathe without spoilage. Shellac is used as a stiffener for felt hat bodies, primarily for recreational hats. It is also used to stiffen playing cards, providing "snap."

### Economic Aspects

Rosin and its derivatives are economically the most important natural resins. Approximately  $1150 \times 10^3$  metric tons of these materials are produced annually and sold throughout the world. The principal producers are the People's Republic

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of China (ca 40%) and the United States (ca 25%), followed by Russia. Most of the remainder is produced in Indonesia, Portugal, Finland, India, Brazil, and Mexico. In 1996, the lowest grades of rosin were priced at \$750/t. Most rosin is converted to its many derivatives to meet requirements for industrial applications. The principal producers of rosin derivatives are Arizona Chemical Company, Hercules Incorporated, Westvaco, Union Camp, and Georgia-Pacific.

The traditional natural resins are collected or isolated from trees, primarily in the more moderate climates of the world. Before World War II, annual consumption of these resins in the United States was about 18,000–23,000 t. This dropped to about 9000 t/yr by the late 1940s. The total imported volume in 1995 is estimated at <500 t. These resins have been replaced by synthetic resins in most industrial applications. Traditional natural resins are sold in bulk quantities for about \$1.32–\$6.60/kg. Special grades of these resins are sold for as much as \$132/kg. The largest importer of traditional natural resins is P. L. Thomas & Company, Inc.

Shellac has had a commercial history similar to that of the traditional resins. It has been replaced by synthetic resins in many applications. In the 1950s, about 19,000 t of various grades of processed shellac were available in the United States. The volume was about 5,500 t in 1995. The largest importer of shellac is William Zinsser & Company, Inc. The superior grades of shellac are sold for about \$6.60–\$9.90/kg, depending on quality.

### Health and Safety Information

Rosin has a low order of toxicity following ingestion or skin contact. Rosin and its numerous derivatives have a number of permitted food packaging and other direct and indirect food contact uses throughout the world. Sanctioned uses applicable in the United States are outlined in U.S. Food and Drug Administration (U.S. FDA) Regulations (2). Material Safety Data Sheets (MSDSs) for specific rosins and their derivatives should be consulted before their use.

Natural resins such as dammar and Manila copal have been described in U.S. FDA Regulations (3). The Material Safety Data Sheets for these products issued by the importer describe them as nontoxic and nonallergenic.

Shellac has been affirmed by the U.S. FDA (4) as GRAS for food applications. The most significant uses for shellac are in food, for coating fruits and confections to preserve quality and appearance.

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